THE STRUCTURE AND PROPERTIES OF SOME METAL DERIVATIVES OF AZO AND AZO-METHINE DYES

BY

GUNTHER LOUIS EICHHORN

B.A., University of Louisville, 1947
M.S., University of Illinois, 1948

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Introduction

The fruitfulness of the coordination theory, as conceived by Werner and extended by many others, lies in its wide applicability to problems of chemical constitution that have defied solution by the use of other tools. Among the substances whose structures have been interpreted by the utilization of this theory are the so-called metal "lakes" of the azo and azo-methine dyes. An analysis of past investigations of these materials (1) leaves no doubt that they are true coordination compounds, and that the azo and azo-methine groups are, therefore, capable of acting as coordinating electron donors.

The present study represents a two-pronged attack upon these dye "lakes." The first objective is the further elucidation of the chemistry of these substances by investigations of the dye - complex equilibria, and by the preparation of hitherto unknown dye complexes. The second and perhaps the more important objective is the extension of the coordination theory by examination of the behavior of azo and azo-methine dye complexes tailor made to test certain aspects of coordination. The realization of the latter goal has led to the following two conclusions:

1) Coplanarity of the coordinating agent appears to be more important than complete cyclization in the stabilization of inner complexes such as the porphyrins and the phthalocyanins.
2) Coordination with a positive ion may result in the decomposition of the coordinating agent.

Experimental and Discussion

I. *Ortho-Hydroxy Azo Dye Complexes*

Two series of experiments were conducted to test the

equilibria existing between the complexes of benzene-azo-β-naphthol and their dissociation products, the free dye and the metal ions. In one series equimolar mixtures of the dye, copper acetate, and nickel acetate, were allowed to react in hot ethyl alcohol. The ratio of nickel to copper in the insoluble mixture of complexes was 0.783, indicating the extent of reaction of the dye with the two competing metal ions.

In the other series weighed amounts of the copper complex were subjected to the action of varying concentrations of perchloric acid. It was found that the extent of decomposition was not governed by a constant ratio between the concentration of copper and the square of the hydrogen ion concentration, as anticipated from the equilibrium expression, but depended, instead, upon the amount of complex in contact with the solution. Apparently only the molecules of complex on the surface of the solid particles take part in the heterogeneous reaction.

Meta-phenylene-bis-azo-β-naphthol, which may be considered a bifunctional benzene-azo-β-naphthol, was prepared according to Schoutissen (2). It formed a 1:1 complex with copper, revealing that both azo groups and both hydroxy groups must act as coordinating donors.

II. *Azo and Azo-methine Dye Complexes Related to the Porphyrins*

The inner complex porphyrins and phthalocyanins represent the maximum in complex stability that has been achieved so far. In addition to the usual structural characteristics of very stable complexes, these substances boast complete coplanarity, and an entirely closed organic ring structure enveloping the several chelate rings. In the present investigation these two factors were separated in a reaction which could result in the formation of a product exhibiting either one or the other of these properties, but not both of them simultaneously.

2-hydroxy-isophthalaldehyde* was allowed to react with ethylenediamine and nickel acetate in a water - alcohol solution. Analysis of the product as well as magnetic measurements and chemical behavior, showed that it was the nickel complex of the Schiff's base produced by the condensation of *one* molecule of ethylenediamine with two of the aldehyde. This complex, containing two free aldehyde groups, is capable of existing in a coplanar configuration. All efforts to force a *second* molecule of ethylenediamine to span the remaining aldehyde groups proved to be in vain. If such a bridge had been established, the nickel ion would have formed the nucleus of a six - chelate ring system, completely surrounded by an organic ring structure, but the coplanarity of the molecule would have been destroyed. Evidently coplanarity is the more important of the two factors in furnishing stability to such substances,

III. *The Mechanism of the Decomposition of Anil Complexes*

The formation of chelate rings involving the azo and azomethine linkages as coordinating groups has been observed in the presence of hydroxy, amino, and carboxy groups, and heterocyclic nitrogen atoms, in a position ortho to the attachment of the chromophoric group. It was considered of interest to study examples of compounds in which the other complexing group would be a heterocyclic sulfur atom; for this purpose the condensation products of 2-thiophenaldehyde* with ortho-amino phenol and with ethylenediamine were prepared and characterized. The metal complexes of these Schiff's bases could not be obtained, however, under the usual "lake" forming conditions.

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* The synthesis of this compound by different methods had been previously claimed by Voswinckel (3) and by Weil and Brimmer (4), who reported melting points of 88° and 125°, respectively. Repetition of Voswinckel's procedure, and the subsequent application of methods of purification, resulted in the isolation of Weil and Brimmer's 125° substance.

* The author is indebted to Dr. Seymour Meisel and Dr. D. E. Badertscher, of the Socony Vacuum Oil Co., Paulsboro, N. J., for furnishing the 2-thiophenaldehyde used in these studies.

The system copper sulfate - bis-thiophenal-ethylenediamine (sn) was then studied by the method of continuous variations; the presence of 1:1 and 1:2 complexes was indicated in this manner. These substances were subsequently isolated in the solid state, and analysis proved their identity as $[Cu\ en\ (H_2O)_2]SO_4$ and $[Cu\ en_2]SO_4$ (en = ethylenediamine). The copper chloride - ethylenediamine system had been studied previously by Jonassen and Dexter (5); our results checked theirs completely. It has thus been shown that the heterocyclic sulfur atom in this case does not contribute to the formation of a stable chelate ring, since the Schiff's base is actually decomposed in the presence of the metal ions.

The mechanism of this decomposition was elucidated by observations of the changes in absorption of 1:1 and 1:2 copper sulfate - sn solutions. Evidence for the short-lived existence of $[Cu\ sn\ (H_2O)_2]^{+2}$ and $[Cu\ sn_2]^{+2}$ was gathered from the presence in the freshly prepared mixtures of ions more highly absorbing in the visible spectrum than $[Cu\ en\ (H_2O)_2]^{+2}$ and $[Cu\ en_2]^{+2}$.

The rates of decomposition of the copper -sn complexes into the ethylenediamine complexes were determined. It was found that the decomposition of the 1:1 complex followed first order kinetics, as anticipated for the formation of $[Cu\ en\ (H_2O)_2]^{+2}$ from $[Cu\ sn\ (H_2O)_2]^{+2}$. The behavior of the 1:2 complex system suggested that the mechanism of its decomposition involves two steps, in which $[Cu\ sn\ en]^{+2}$ is produced as an intermediate. Studies in the ultraviolet region of the spectrum indicate that two moles of hydrogen ion produce the same extent of decomposition as one mole of copper. That the decomposition of the Schiff's base in coordination with copper is not due to the drop in pH associated with the addition of copper sulfate to the solution is evident from the similar behavior encountered when acetate is substituted for the sulfate. It appears, therefore, that the severance of the carbon to nitrogen bonds is the direct result of the formation of a stronger bond between nitrogen and a

positive ion. In harmony with this conclusion is the fact that nickel ion apparently causes a similar dissociation.

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VITA

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